学位申請論文

山本直一

主論文 1

The Magnetic Properties of the Synthetic Iron Oxyhydrates

Naoichi YAMAMOTO*

主論文

The formation and the magnetic properties of ferric oxide, ferric oxyhydrates and their fine particles.

(酸化鉄、オキシ水酸化鉄及びこれら微粒子の生成と磁性)

第1部; The Magnetic Properties of the Synthetic Iron Oxyhydrates

(合成されたオキシ水酸化鉄の磁気的性質)

第2部; The Particle Size Dependence of the Néel Temperature of α-FeOOH

(α-FeOOH 微粒子のネール温度の粒度依存性)

第3部; The Shift of the Spin Flip Temperature of α-Fe_2O_3 Fine Particle

(α-Fe_2O_3 微粒子のスピンフリップ温度の移動)

(Bulletin of the Institute for Chemical Research, Kyoto University 46 (6), 1968)

The Magnetic Properties of the Synthetic Iron Oxyhydrates

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Received September 24 , 1968

Pure and large crystals of three modifications of the α-, β- and γ-FeOOH were synthesized and their magnetic properties were studied. These iron oxyhydrates were antiferromagnetic with the Néel temperature being 400°K, 273°K and 50°K for α-, β-and γ-FeOOH, respectively. The direction of the electron spin axis was found from the Mössbauer effect to be parallel to the c-axis of the crystals for all these iron oxyhydrates.

INTRODUCTION

Three modifications of the iron oxyhydrate, α-, β- and γ-FeOOH, are known. Mineral names of α- and γ-FeOOH are goethite and lepidcrocite. The crystal structures of α- and γ-FeOOH are orthorombic, belonging to the space groups of Pbnm and Bbmn, respectively.[1,2] The crystal structure of β-FeOOH is tetragonal or pseudotetragonal.[3] In these compounds, however, positions of the hydrogen atoms have not been determined.

In recent years many Mössbauer and other magnetic studies have been done on these iron oxyhydrates.[4)~12)] However, the published data on β- and γ-FeOOH are still few. As to α-FeOOH, there are great discrepancies between the results published on temperature dependence of the magnetic susceptibility, Mössbauer spectrum and Néel temperature. These discrepancies may be attributed to the difference in chemical purity and particle size between the samples used in the measurement.

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The present work reports the magnetic susceptibility measurement of the iron oxyhydrates which are as pure and large as possible in the synthetic specimen and the spin structures determined by the Mössbauer effect analysis.

EXPERIMENTAL

(I) Sample Preparation

1. α-FeOOH

The samples of α-FeOOH were prepared as follows.

(a) Stamped powder of the electrolytic iron, 31.5g in weight was poured into 1ℓ of 0.125M-H_2SO_4 solution. The solution containing the iron powder was oxidized by bubbling the air therein at the rate of 1000ℓ per hr at 70°C. After all of iron powder was oxidized, the resultant yellow precipitate was filterd, washed with distilled water and dried at 90°C.

(b) 500g of $FeSO_4$ $7H_2O$ was dissolved in 2ℓ of disstilled water and after 1ℓ of 6N-NaOH solution was added diluted to 3.5ℓ with distilled water. The alkaline suspension containing $Fe(OH)_2$ precipitate was oxidized at 40°C by bubbling the air therethrough.

After 60 hr $Fe(OH)_2$ was oxidized perfectly and converted to α-FeOOH precipitate. The precipitate was filtered, washed with water and dried at 90°C.

2. β-FeOOH

500g of $FeCl_2.nH_2O$ and 100g of NH_4Cl were dissolved in 3ℓ of distilled water. The solution was oxidized by bubbling the air at the rate of 200ℓ per hr at 70°C. After 5 hr of this procedure, yellow colored precipitates, the mixture of α-FeOOH and β-FeOOH were deposited in the vessel. In this stage pH value of the solution was about 1.2. The yellow precipitate was separated from the solution by filtration. The filtrate was again oxidized at the same condition as above for 60 hr. The precipitate thus obtained from the second solution was pure β-FeOOH. After filtration the precipitate

was subjected to electrodialysis to get off Cl^- ions contaminating in the crystal lattice.

3. γ-FeOOH

(a) Stamped powder of electrolytic iron, 50g in weight, was poured into 500ml of 0.15M acetic acid solution. The suspension was oxidized by bubbling the air at the rate of 1000ℓ per hr at 50°C. After 7 hr iron powder was perfectly consumed and orange yellow precipitate of γ-FeOOH was deposited.

(b) 500g of $FeCl_2.nH_2O$ was dissolved in 2ℓ of the distilled water and to this solution was added the alkaline solution in the amount of 0.4 equivalents of the acid radical. After total volume of the solution was diluted to 3.5ℓ with water, the resultant white suspension was oxidized by bubbling the air for 50 hr at 20°C. The precipitate of γ-FeOOH thus obtained was filtered, washed with water and dried at 90°C.

The precipitates of α-, β- and γ-FeOOH obtained in this way were affirmed by X-ray diffraction patterns and infrared spectra to be pure specimens. Impurity contents were checked with usual chemical methods. As an example the analytical result of α-FeOOH prepared by the first method is given in Table 1. Chemical analysis proved that these samples were extremely pure and reliable in the magnetic measurement.

The particle shapes and sizes of these iron oxyhydrates were observed on the electronmicrographs. Fig. 1, 2 and 3 are electronmicrographs of α-, β- and γ-FeOOH particles, respectively.

(II) Magnetic Measurements

Magnetic susceptibility, χ was measured with an ordinary magnetic torsion balance above the liquid nitrogen temperature and by A-C Hartshorn bridge method from liquid helium temperature to liquid nitrogen temperature. Mössbauer effect was measured with the TMC multichannel type apparatus.

RESULT AND DISCUSSIONS

(I) Magnetic Susceptibility

In Fig. 4 the temperature dependence of χ of three iron oxyhydrates are given. χ of α-FeOOH was measured from 1.2°K to 440°K, where α-FeOOH decomposes to α-Fe_2O_3. χ shows the value of 46 x 10^{-6} c.g.s.e.m.u. at room temperature and exibits no temperature dependence. As previously reported, the Néel temperature of this sample was determined to be 400°K from the temperature dependence of the internal field of the Mössbauer spectrum.

χ of β-FeOOH is also temperature independent and the value is 25 x 10^{-6} c.g.s.e.m.u. The Néel temperature of this compound was found to be 273°K both from the temperature dependence of the internal field of the Mössbauer spectrum and by the thermal differential analysis. This value is in good agreement with the value reported by Dézsi et al.[10)]

χ of γ-FeOOH is 40 x 10^{-6} c.g.s.e.m.u. at room temperature and small broad peak was observed at near 50°K. As shown on the Mössbauer spectrum in Fig. 5, the magnetic hyperfine splitting is observed at liquid helium temperature. It should be noted that only quadrupole splitting was shown on the previously reported spectrum at liquid nitrogen temperature. These result confirms that γ-FeOOH is antiferromagnetic below 50°K.

χ of a single crystal of mineral goethite was reported by Oosterhout, properties of which may be representative of those of a Heisenberg antiferromagnet with $S=\frac{5}{2}$. On the other hand temperature dependence of χ observed in the present experiment was different from that of normal antiferromagnet of a powder specimen, that is, χ showed no peak at the Néel temperature and was temperature independent below the Néel temperature. These curious magnetic behaviours, which are observed also in the case of β-FeOOH, seem to be caused by some kind of the size effect although

precise discussion is impossible. Theoretical explanation of the temperature independent χ of γ-FeOOH above the Néel temperature is also obscure.

(II) Spin Structures

The spin structures of these iron oxyhydrates were determined by the Mössbauer effect with utilizing the strong anisotropic particle shapes of the samples. The angular dependences of the Mössbauer transition probabilities are expressed as $9/4(1+\cos^2\theta)$ for peak 1 and $6.3\sin^2\theta$ for 2 and $5,3/4(1-\cos^2\theta)$ for peak 3 and 4, where θ represents the angle between the incident gamma ray and the magnetic hyperfine field direction and the peak number is given in the order from the lower to the higher energy peak. In the case where magnetic hyperfine field direction is random against incident gamma ray, relative peak intensities of six peaks will become 3:2:1:1:2:3. When the direction of the magnetic hyperfine field is parallel or perpendicular to the incident gamma ray, the relative intensities will be 3:0:1:1:0:3 or 3:4:1:1:4:3. Therefore, if the correlation between the crystal axis and the incident gamma ray is given, the relative peak intensities of the Mössbauer spectrum make it possible to determine the spin axis of the sample.

As shown in Fig. 1, 2 and 3 the particle shapes of the iron oxyhydrates are acicular. Because of these crystal shapes the samples are easily inclined to take such anoriented state as the longest axes are in a plane. Previous electron-microscopic studies clarified the longest axis of a particle is in coincidence with the crystal c-axis in each iron oxyhydrate.[13,14,15)]

In practice oriented samples were made as follows. The oxyhydrates were suspended in water and the suspensions were filtered slowly through the Membran filteres. After drying the samples, these were pressed with uniaxial pressure of 10^3 kg/cm^2. Random oriented samples were made by mixing

powder well with silicone grease. The relative peak intensities of the X-ray powder pattern showed that the c-axis of a sample was in good oriented state, perpendicular to the pressed direction. The preferred oriented sample was set so as for the pressed plane of the sample to be perpendicular to the incident gamma ray.

In Fig. 5 is given the spectra of α-FeOOH at room temperature. The spectrum of the random oriented sample has the ratio of the peak intensities of 3:2:1:1:2:3, the expected value of the completely random sample, whereas the ratio of the peak intensities observed on the preferred oriented sample is close to the value of 3:4:1:1:4:3. In such a sample that all the c-axes of particles are in same plane but other a- and b-axes are completely random, the observed ratio of the peak intensities is obtained only when the spin axis is perpendicular to the incident gamma ray. It is obvious from the simple calculation another spin arrangement will give same spectrum which is observed in the random oriented case. Therefore the antiferromagnetic spin axis of α-FeOOH is parallel to the c-axis. The result is in good agreement with that of Oosterhout who determined the spin axis to be parallel to the c-axis from the temperature dependence of the magnetic susceptibilities perpendicular and parallel to the c-axis, using the mineral single crystal specimen.

The relation of Mössbauer spectra with the particle orientation can be discussed quite analogously with the previous case of α-FeOOH. From the observed Mössbauer spectrum it is concluded that the spin axes of β- and γ-FeOOH are parallel to the c-axes in both compounds. Mössbauer spectra of β- and γ-FeOOH are shown in Fig. 6 and 7, at liquid nitrogen and liquid helium temperature, respectively.

CONCLUSION

It is apparent from the above experimental results that three kinds of iron oxyhydrates α-, β- and γ-FeOOH are antiferromagnets, and spin axis of each compound is parallel to the crystal c-axis. Other results are summarized in Table 2. The magnetic susceptibilities of these samples show somewhat peculiar behavior, but satisfactory explanation of which is not given at the present time.

ACKNOWLEDGEMENT

The author would like to thank Prof. T. Takada for prominent guidance during the course of this work. He also wishes to thank Drs. Y. Bando, M. Kiyama and T. Shinjo for fruitful suggestions and discussions.

REFERENCES

1) Wyckoff, Crystal Structure, John Willey and Sons, 1 291, 293.

2) J.D. Bernal, D.R. Dasgupta and A.L. Mackay; Clay Minerals Bull., 4 15 (1959).

3) M.J. Rossiter and E.A.M. Hadgson, J. Inorg. Nuclea. Chem. 27, 63 (1965).

4) F. Van der Woode and A.J. Dekker, Phys. Stat. Soc., 13, 181 (1966).

5) A.Z. Hrynkiewicz and D.S. Kulganezuk, Acta. Phys. Polo., 24, 689 (1966).

6) A.Z. Hrynkiewicz, D.S. Kulganezuk and K. Termala, Phys. Letters (Netherlands) 17, 93 (1965).

7) G.E. Van Oosterhout, Proc. Int. Con. on Magnetism, Nottingham England September 1964.

8) A. Szytuza, A. Burewicz, K. Dyperk, A. Hrynkiewicz, D. Kulganezuk, Z. Obuszko, H. Rzany and A. Wanic, Phys. Stat. Sol., 17, K195 (1966).

9) T. Takada, M. Kiyama, Y. Bando, T. Nakamura, M. Shiga, T. Shinjo, N. Yamamoto and Y. Endo, J. Phys. Soc. Japan 19. 1744 (1964).

10) I. Dézsi, L. Keszthelyi, D. Kulganezuk, B. Mcinr, and N.A. Eissa, Phys. Stat. Sol., 22, 617 (1967).

11) M.J. Rossiter and E.A.M. Hadgson, J. Inorg. Nuclea. Chem. 27, 63(1965).

12) C.L. Herzenberg and D. Tomas, J. Geophys. Res. 71, 2661 (1966).

13) J.H.L. Watson and P.R. Cardell Jr., J. Phys. Chem., 66, 1757 (1962).

14) T. Takada, M. Kiyama and S. Shimizu, Bull. Inst. Chem. Res., Kyoto Univ., 42, 505 (1964).

15) G.E. Van Oosterhout, Acta. Cryst., 13, 932 (1960).

Figure Captions

Fig. 1 Electronmicrographs of α-FeOOH, acicular shape of the particles is shown.

Fig. 2 Electronmicrograph of β-FeOOH.

Fig. 3 Electronmicrographs of γ-FeOOH.

Fig. 4 Temperature dependence of the magnetic susceptibilities of three iron oxyhydrates.

Fig. 5 Mössbauer spectra of α-FeOOH at room temperature, preferred oriented sample (above) and random oriented sample (below).

Fig. 6 Mössbauer spectra of β-FeOOH at liquid nitrogen temperature, preferred oriented sample (above) and random oriented sample (below).

Fig. 7 Mössbauer spectra of γ-FeOOH at liquid helium temperature, preferred oriented sample (above) and random oriented sample (below).

Table 1. Impurity Contents of α-FeOOH
(prepared by the first method)

Impurities	Atomic %
Si (as SiO_2)	< 0.01
S (as SO_3)	< 0.5
Mn (as Mn_2O_3)	< 0.01
Co (as Co_3O_4)	< 0.01
Cu (as Cu_2O)	< 0.01

Table 2. Observed values of the magnetic hyperfine splitting, quadrapole splitting, isomershift and Neel temperature of α-, β-, γ-FeOOH

samples	magnetic hyperfine splitting at liq He temp.	quodrupole splitting (paramagnetic state)	isomer shift	Néel temperature	spin axis
α-FeOOH	530KOe	0.60mm/sec.	0.5mm/sec.	400°K	(001)
β-FeOOH	490KOe	0.60mm/sec.	0.56mm/sec.	273°K	(001)
γ-FeOOH	470KOe	0.51mm/sec.	0.5mm/sec.	50°K	(001)

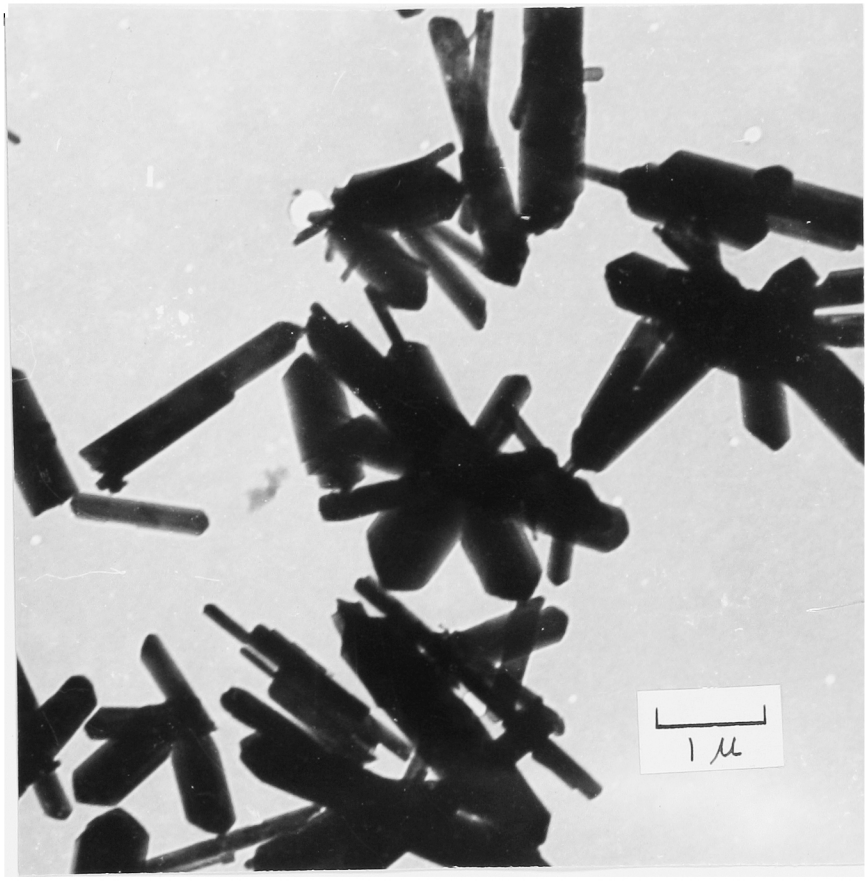

Fig. 1 Electronmicrographs of α-FeOOH, acicular shape of the particles is shown.

Fig. 2 Electronmicrograph of β-FeOOH.

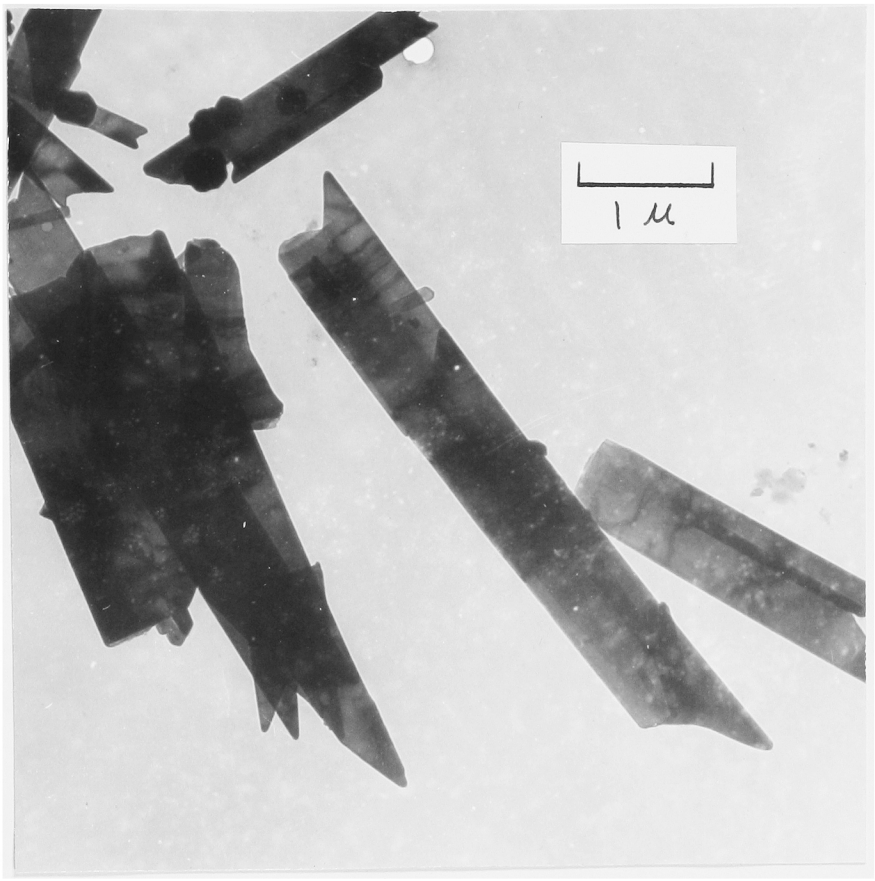

Fig. 3 Electronmicrographs of γ-FeOOH.

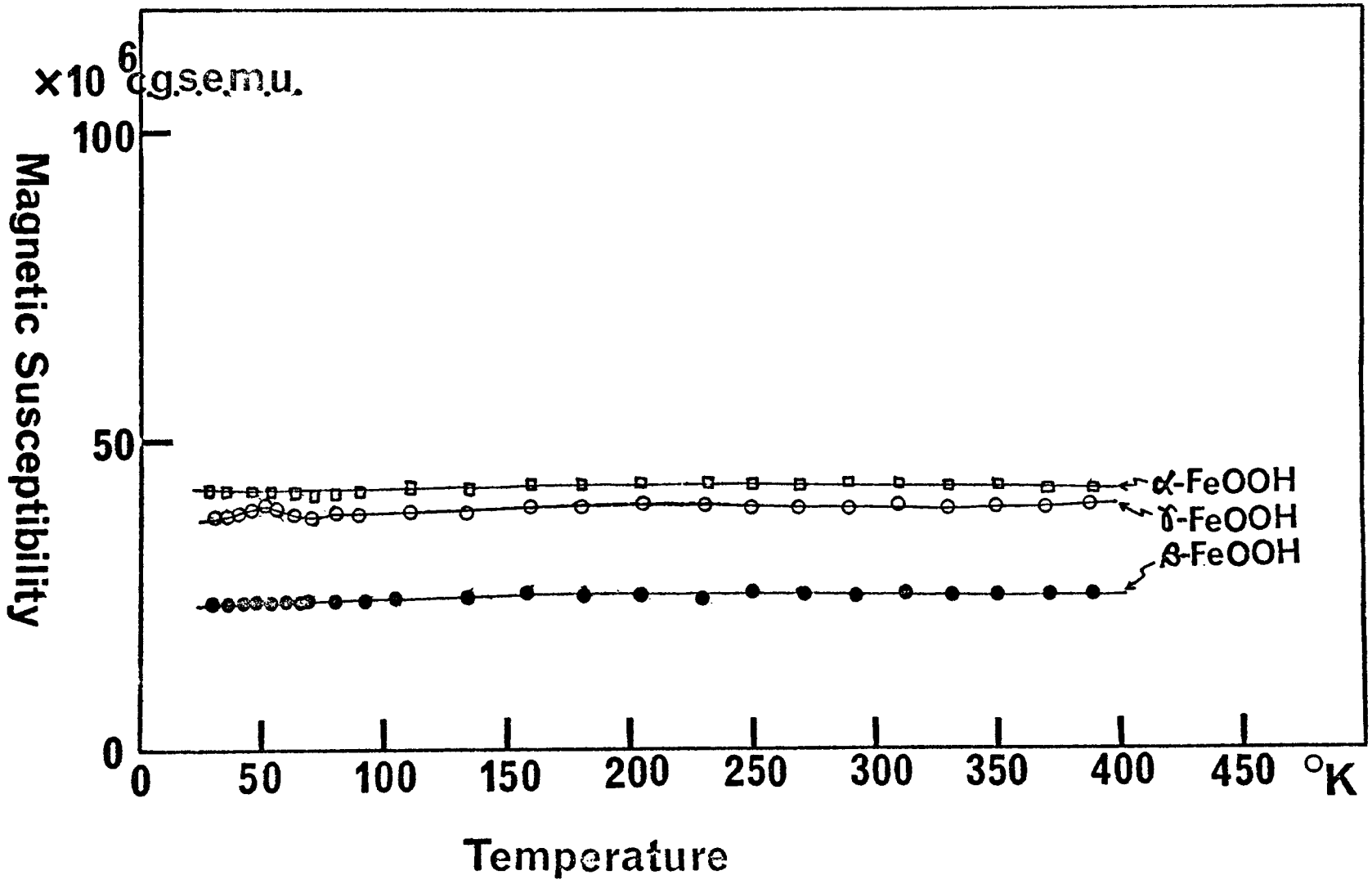

Fig. 4 Temperature dependence of the magnetic susceptibilities of three iron oxyhydrates.

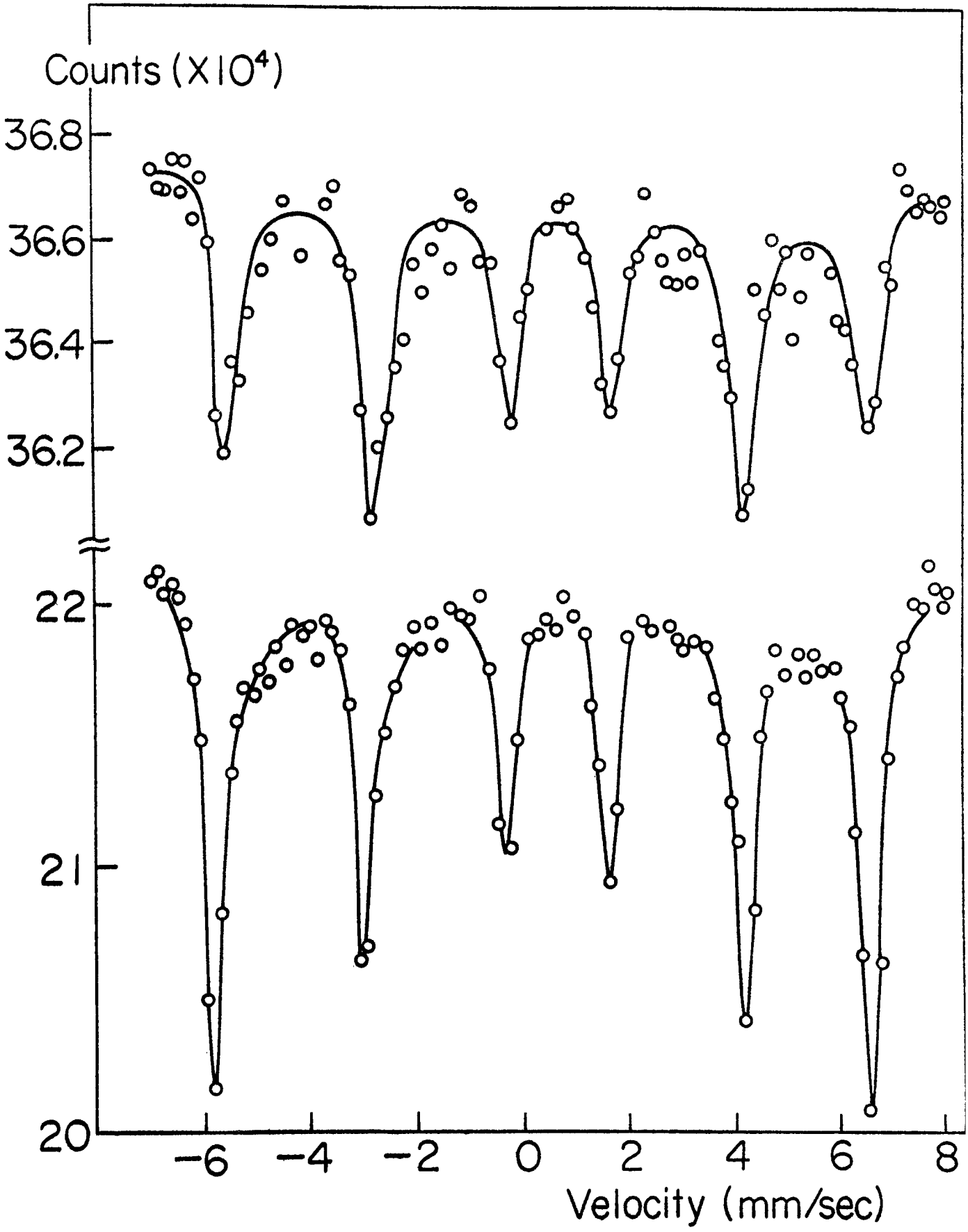

Fig. 5 Mössbauer spectra of α-FeOOH at room temperature, preferred oriented sample (above) and random oriented sample (below).

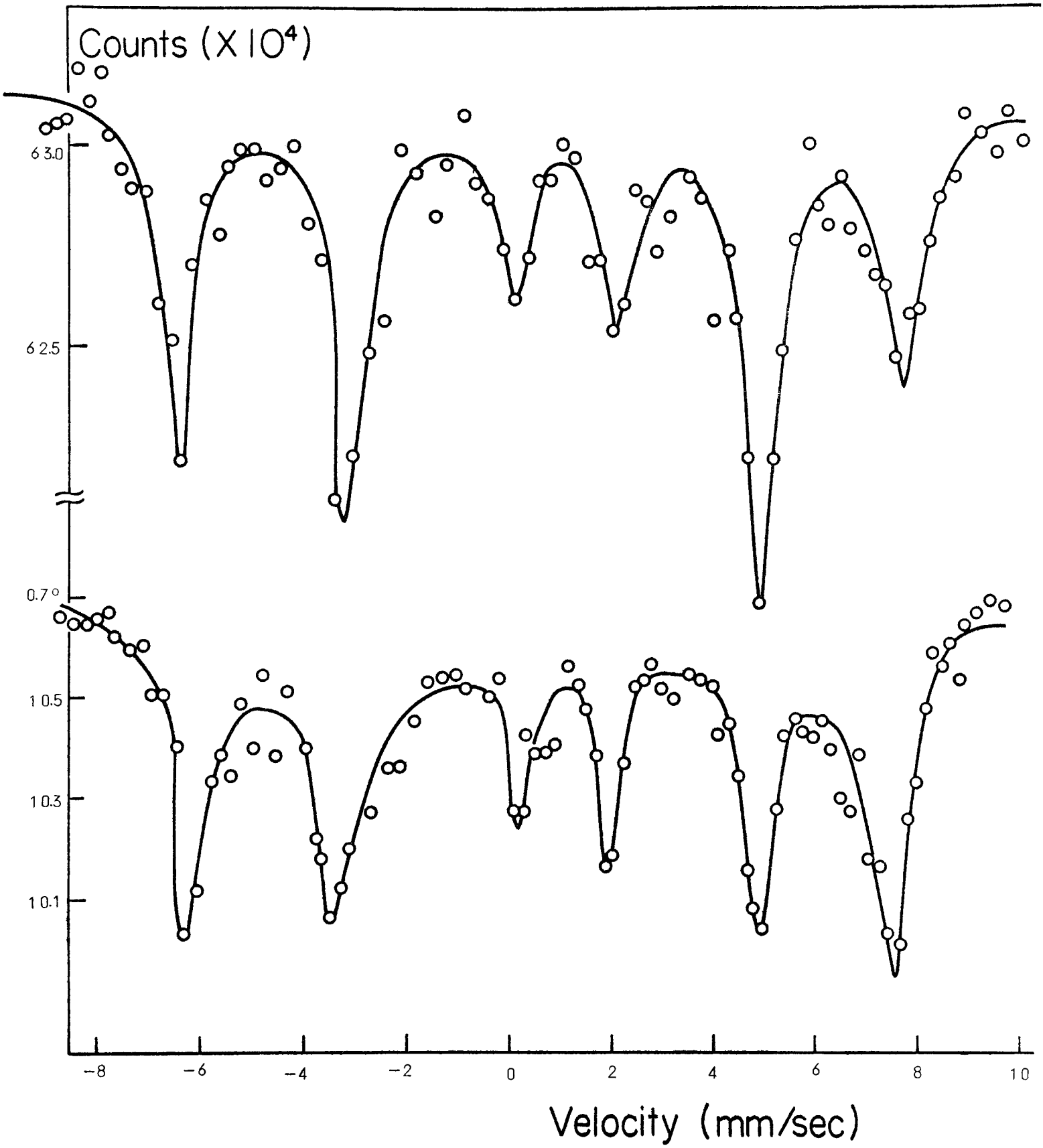

Fig. 6 Mössbauer spectra of β-FeOOH at liquid nitrogen temperature, preferred oriented sample (above) and random oriented sample (below).

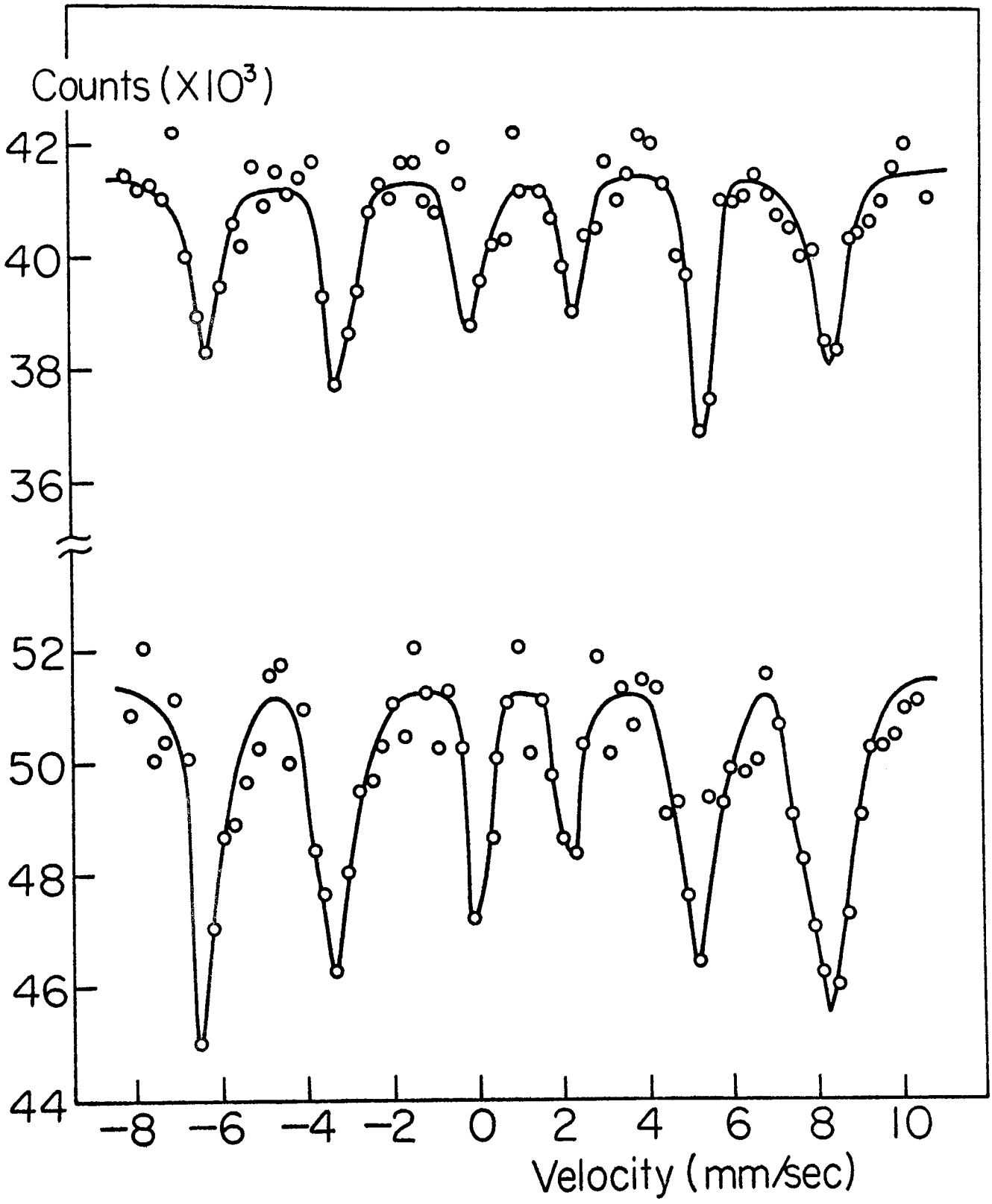

Fig. 7 Mössbauer spectra of γ-FeOOH at liquid helium temperature, preferred oriented sample (above) and random oriented sample (below).

主論文 2

The Particle Size Dependence of the Néel Temperature of α-FeOOH Fine Particles

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(Bulletin of the Institute for Chemical Research, Kyoto University 46 (6), 1968)

The Particle Size Dependence of the Néel Temperature of α-FeOOH Fine Particles

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Received September 24, 1968

The particle size dependence of the Néel temperature of α-FeOOH was studied experimentally. The Néel temperature decreased with decreasing particle size and the α-FeOOH of 2000Å in particle size showed the Néel temperature which was about 9% lower than that of the bulk specimen.

INTRODUCTION

In recent years α-FeOOH has been the subject of the Mössbauer and other magnetic studies. There are, however, great discrepancies between the experimental results. The Néel temperature of this compound, determined from the magnetic susceptibility or from the temperature dependence of the internal field, spreads over the wide temperature range. Szytuza et al reported 330°K[1] as the Néel temperature, whereas 440°K was given by Oosterhout[2]. The previously reported values of the Néel temperature was summarized in Table 1.[3,4] It was suggested by some authors that the discrepancy may be due to the deffect structure in the samples. However, clear explanation has not been given yet. In this work the dependence of the Néel temperature on the particle size of α-FeOOH was studied with the purpose of elucidating this problem.

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EXPERIMENTAL

1) Sample preparation

Four samples of α-FeOOH were prepared. One sample (A-1) was made by the oxidation of the suspension of Fe metal with the air. Detailed description of reaction method was given in the precedented paper[5]. The other three samples of (A-2, A-3 and A-4) were prepared in the following way.

200g of $Fe(NO_3)_3:9H_2O$ was dissolved in distilled water, then 89g of NaOH was added to the solution. Resultant brown precipitates, which were amorphous in the X-ray analysis, were aged for 24 hr at room temperature. After that the hydrolysis reaction was carried out on these precipitates at 80°C, 95°C and 130°C respectively. With the proceeding of the reaction the amorphous precipitates were gradually converted to yellow precipitates of α-FeOOH. The α-FeOOH precipitates thus obtained were filtered, washed with distilled water and dried at 80°C. X-ray and near-infrared analysis affirmed that these precipitates consisted of α-FeOOH only. No other element than Fe,H and O was detected by chemical analysis.

2) Measurement

The Néel temperature T_N of α-FeOOH was determined by the temperature dependence of the internal field Hi of the Mössbauer spectrum. The magnetic susceptibility measurement was also used as a subsidiary method. Particle size was determined by electron micrography and gas adsorption method (B.E.T. method).

RESULT AND DISCUSSION

In Fig. 1 the temperature dependence of Hi observed in samples of A-2 and A-4 are given. In Fig. 2 some of the spectra of these samples observed at different temperatures 296°K, 340°K and 355°K are shown. Both samples exhibit ordinary temperature dependence of Hi, but nevertheless

the observed absolute values of Hi are different especially in high temperature range. The temperatures, at which the collapse of Hi occurs, are determined to be 395°K and 365°K by the extrapolation, respectively. The temperature dependence of Hi of the samples of A-1 and A-3 shows the same tendency and the collapse of Hi occurs at 400°K and 386°K. The temperature dependences of the magnetization curves of the sample A-1, A-2, A-3 and A-4 are given in Fig. 3. In these curves of two characteristic behaviors are observed. One is the magnetic cooling effect and the other is the appearence of the broad maximum at the different temperatures. For example, sample A-4 shows the peak at 365°K and below this temperature magnetic cooling effect is observed. The temperature where the peak was observed coincided with the temperatures at which collapse of Hi were observed.

In Fig. 4 an electronmicrograph of sample A-2 is given. From this photograph it is seen that α-FeOOH particle have rectangular shape. Regardless of the particle size, the ratio of three edges of the rectangle that are the longest, middle and the shortest is always 10;1;0.3 approximately. In other words, α-FeOOH particles are isomorphous. Hereafter we represent the particle size with the lenght of the longest edge. The average particle size are summarized in the second column of the Table 2. The particle size is the largest (2μ) for sample A-1 and it decreases with increase of the sample number. The smallest particle size (A-4) is 2000Å.

In discussing it must be proved first that the temperature determined by the extrapolation, where the collapse of Hi occurs, is true T_N. In fine particles there exists possibility that thermal fluctuation of the electron spins gives deceptive T_N. This phenomenon, usually observed in the magnetic susceptibility measurement is called superparamagnetism. In the Mössbauer spectrum thermal fluctuation effect was calculated theoretically by Blame and Tjon[6] as a function of the relaxation time.

Otherwise the equation for the size dependence of relaxation time was given by Néel.[7] These two theories indicate that true T_N is obtained by the extrapolation of the temperature vs. Hi curve of the Mössbauer spectrum even if the thermal fluctuation effect exists. This is shown in Fig. 5 shematically. In this figure solid and dotted lines exibit the expected temperature dependence of Hi under the influence of the thermal fluctuation effect in the case of different T_N. From above discussions it is apparent that the temperature determined by the extrapolation gives true T_N. The data summarized in Table 2 show that in these samples T_N decreases with decreasing particle size. In Fig. 6 particle size dependence of T_N is given graphically.

It is concluded from the present experiment that such factors as the contamination by foreign ions and the change of the lattice parameter are discarded and the decrease of T_N is brought out by the decrease of the particle size. Concerning size dependence of the magnetic ordering temperature only few papers were published both in the theoretical and experimental fields. Dresselhaus obtained the exact solution of T_C in the case of Heisenberg ferromagnet of 8 spins in cubic lattice. In this case T_C is about a half of the infinite system of the same lattice. In the case of α-FeOOH the number of the magnetic ions is about 10^4 and so it is impossible to get the exact solution of T_N. Instead of the exact solution it may be possible to explaine this decrease of T_N based on the model adopted in the explanation of the decrease of T_N in dilute ferrites.[9)-11)]

This model assumes that T_N depends on the average number of the magnetic bonds per magnetic ion and the decrease of T_N begins with the substitution of the magnetic ions with nonmagnetic ions. In the case of α-FeOOH vacancy and the surface take the place of the nonmagnetic ions (It seems natural that the density of the vacancy increases with decreasing

particle size from the magnetic data and the surface also increases with decreasing particle size). As an example, in α-FeOOH of 2000Å in size and of 5% vacancy density, T_N is expected to show about 10% lower value than that of the bulk specimen. Further quantitative discussion is impossible, however, because of the difficulties in estimating the amount of the vacancy in the sample.

CONCLUSION

The present study has shown that T_N of α-FeOOH exibites the particle size dependence and the size dependence is one of the origins of wide divergence of T_N reported for this compound.

It seems probable that the size dependence of T_N is as a result of the increasing vacancy and the surface with decreasing particle size and the same effect is expected to occur in the all kinds of magnetic fine particles.

ACKNOWLEDGEMENT

The author would like to thank Prof. T. Takada for prominent guidance during the course of this work. He also wishes to thank Drs. Y. Bando, M. Kiyama and T. Shinjo for fruitful suggestion and discussions.

REFERENCES

1) A. Szytuza, A. Burewicz, K. Dyperk, A. Hrynkiewicz, D. Kulganezuk, Z. Obuszko, H. Rzany and A. Wanic Phys. Stat. Sol. 17 K195 (1966)

2) G.W. Van Oosterhout Porc. Int. Conf. on Magnetism Nottingham, England September (1964)

3) F. Van der Woode and A.J. Dekker Phys. Stat. Sol. 13, 181 (1966)

4) T. Takada, M. Kiyama, Y. Bando, T. Nakamura, M. Shiga, T. Shinjo, N. Yamamoto and Y. Endo J. Phys. Soc. Japan 19, 1744 (1964)

5) to be published Bull. Inst. Chem. Res. Kyoto Univ. (1968)

6) M. Blume, and J.A. Tjon Phys. Rev. 165, 446 (1968)

7) L. Néel, Ann. Geophys. 5, 99 (1949)

8) G. Dresselhaus Phys. Rev. 126, 1664 (1962)

9) M.A. Gilleo Phys. Chem. Sol. 13, 33 (1960)

10) V.P. Polyakov Soviet Phys. solid state 9, 2224 (1968)

11) I. Nowik Phys. Rev. 171, 550 (1968)

Figure Captions

Fig. 1 The temperature dependence of the internal field of Mössbauer spectra of sample A-2 and A-4.

Fig. 2 The observed spectra of sample A-2 and A-4 at 296°K, 340°K and 355°K, respectively.

Fig. 3 The temperature dependence of the magnetization curves of sample A-1, A-2, A-3 and A-4, respectively. The arrow shows the Néel temperature of each sample.

Fig. 4 Electronmicrograph of sample A-2.

Fig. 5 The expected temperature dependence of the internal field under the influence of the thermal fluctuation effect in the case of different Néel temperatures.

Fig. 6 The observed particle size dependence of the Néel temperature.

Table 1 Reported Néel Temperature of α-FeOOH

Reference	Néel Temperature	Method
1)	330°K	Mag. Sus.
1)	320-370°K	Mag. Sus.
2)	440°K	Mag. Sus.
3)	393°K	Möss. effect
4)	400°K	Möss. effect

Table 2 Observed Particle Size and Néel Temperature

Sample	Particle Size	Néel Temperature
A-1	$>1\mu$	400°K
A-2	6000Å	395°K
A-3	4000Å	387°K
A-4	2000Å	365°K

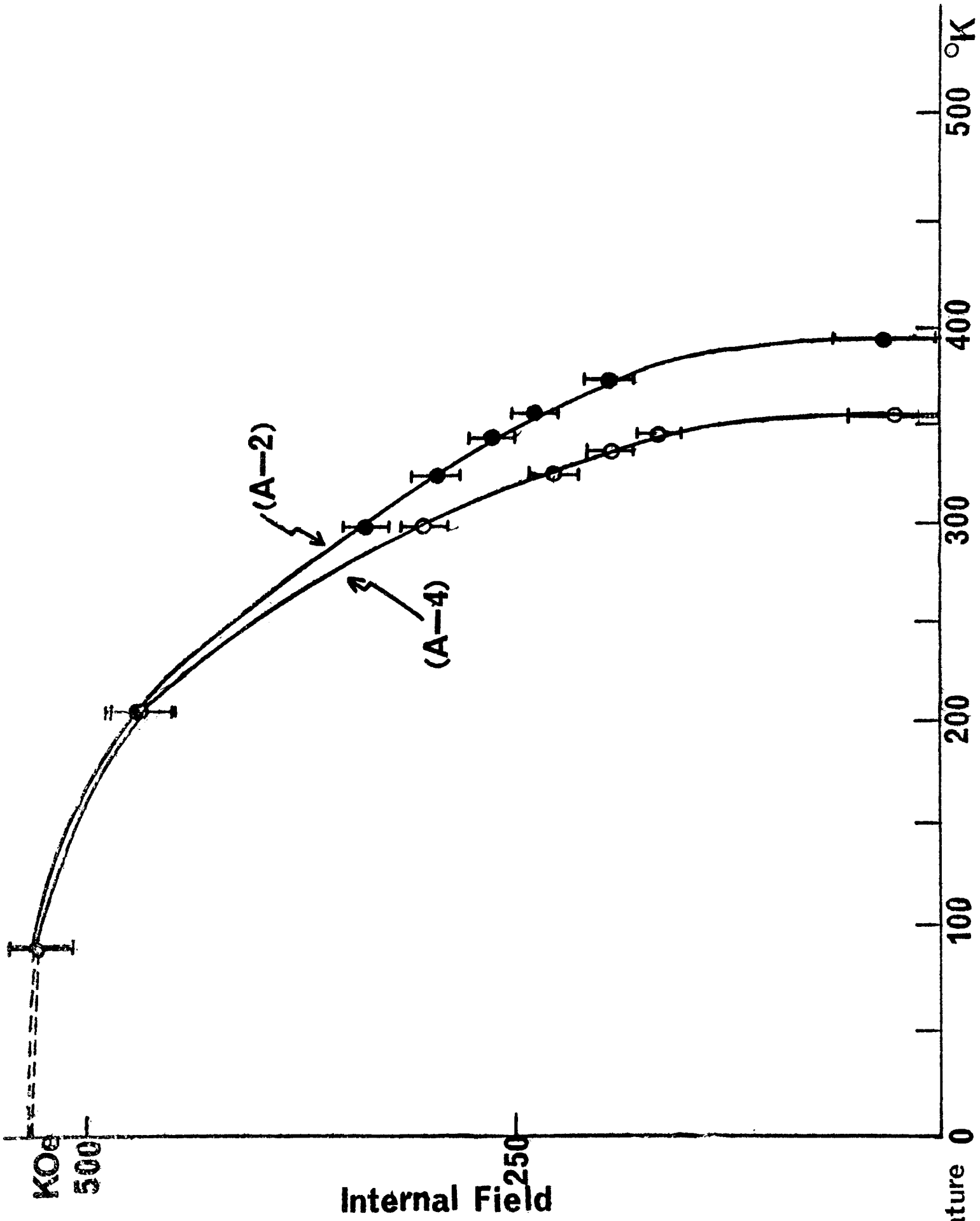

Fig. 1 The temperature dependence of the internal field of Mössbauer spectra of sample A-2 and A-4.

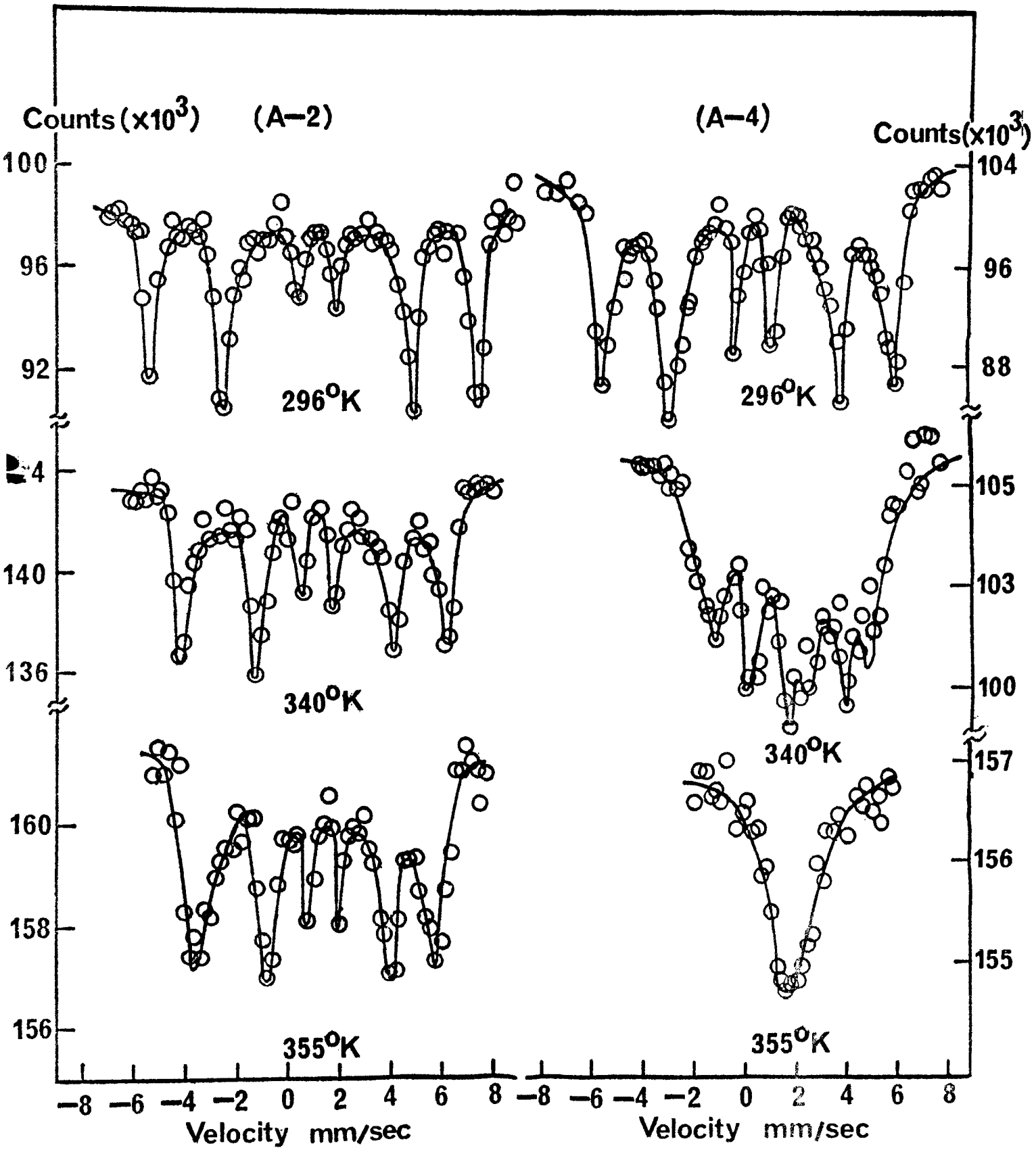

Fig. 2 The observed spectra of sample A-2 and A-4 at 296°K, 340°K and 355°K, respectively.

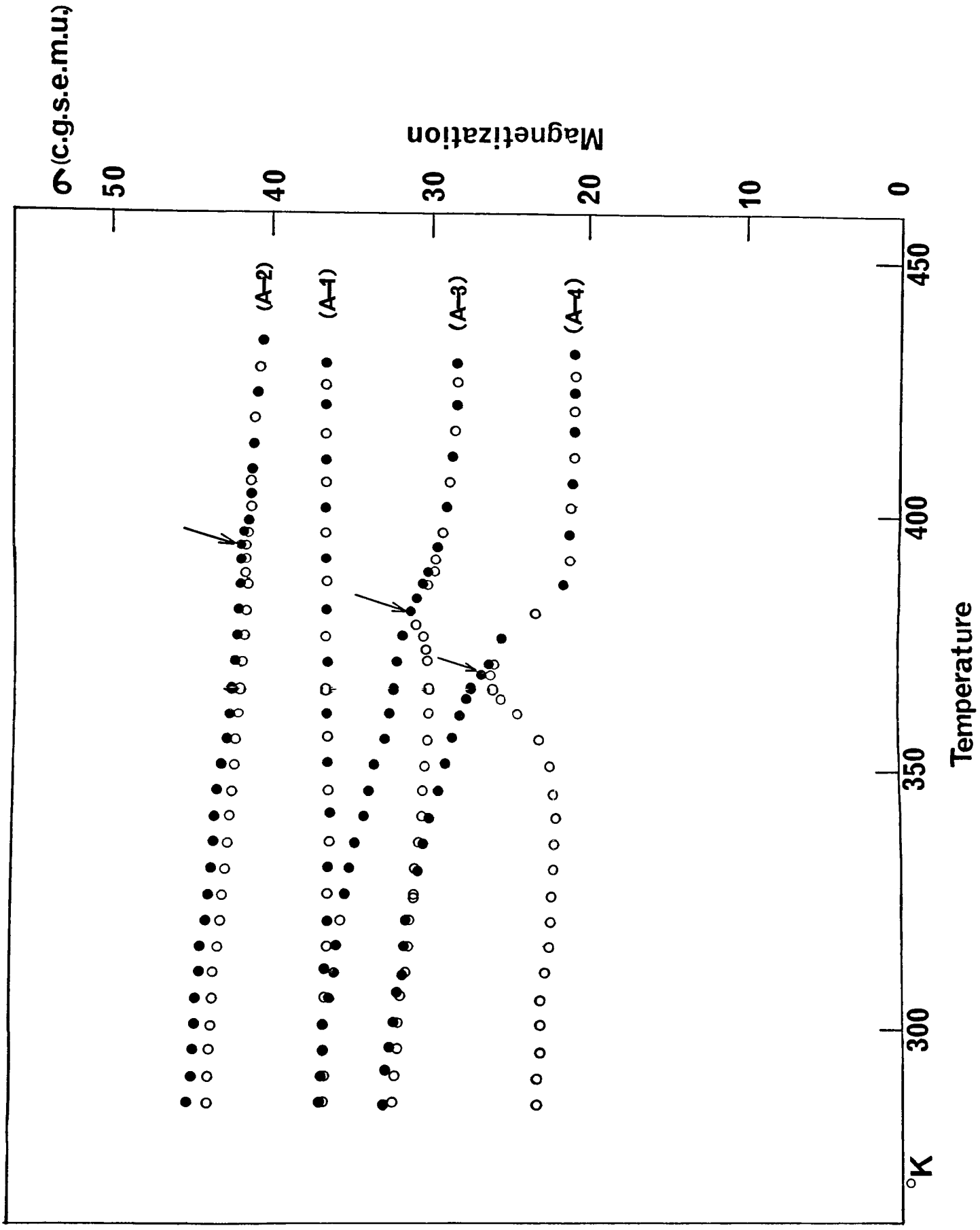

Fig. 3 The temperature dependence of the magnetization curves of sample A-1, A-2, A-3 and A-4, respectively. The arrow shows the Néel temperature of each sample.

Fig. 4 Electronmicrograph of sample A-2.

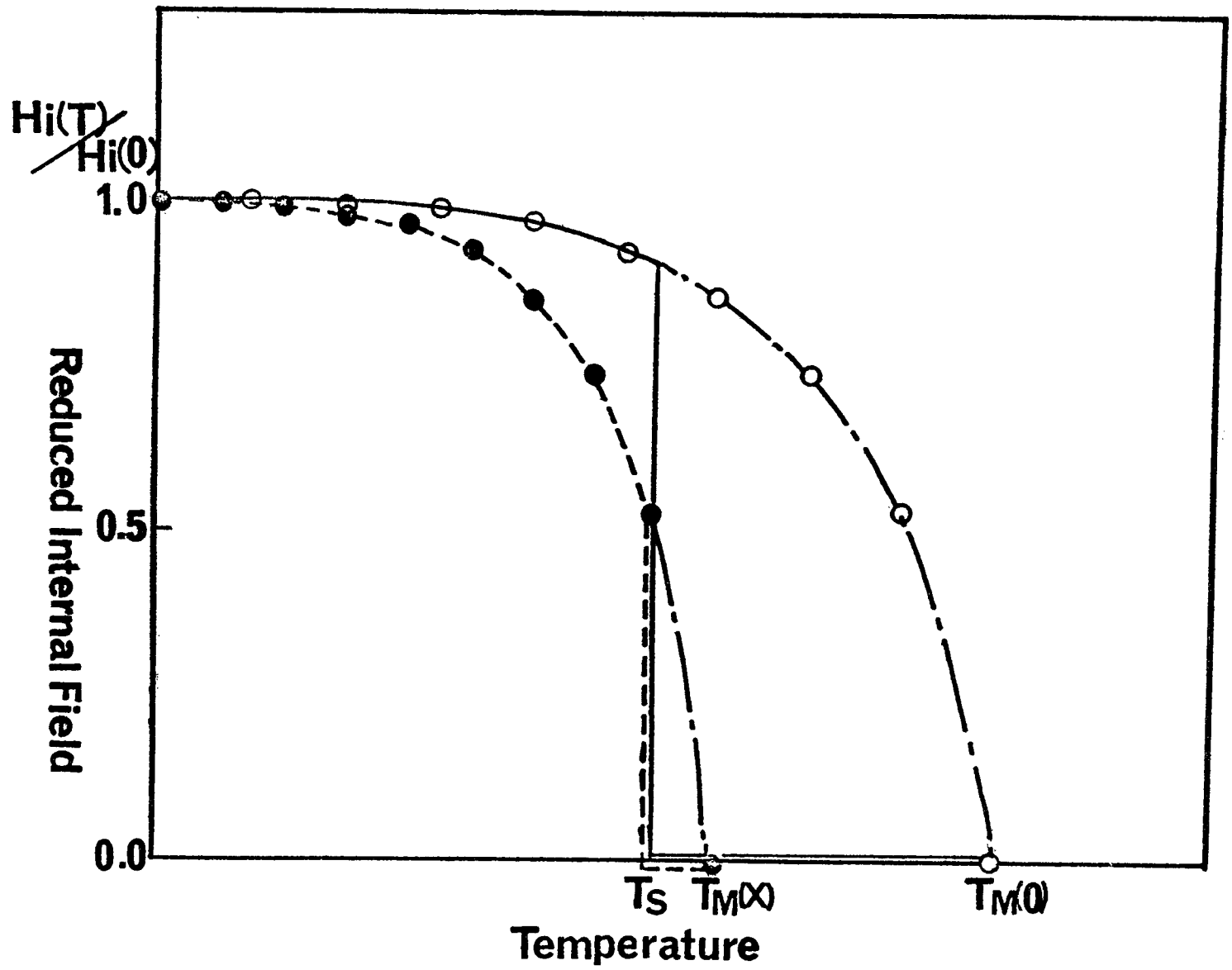

Fig. 5 The expected temperature dependence of the internal field under the influence of the thermal fluctuation effect in the case of different Néel temperatures.

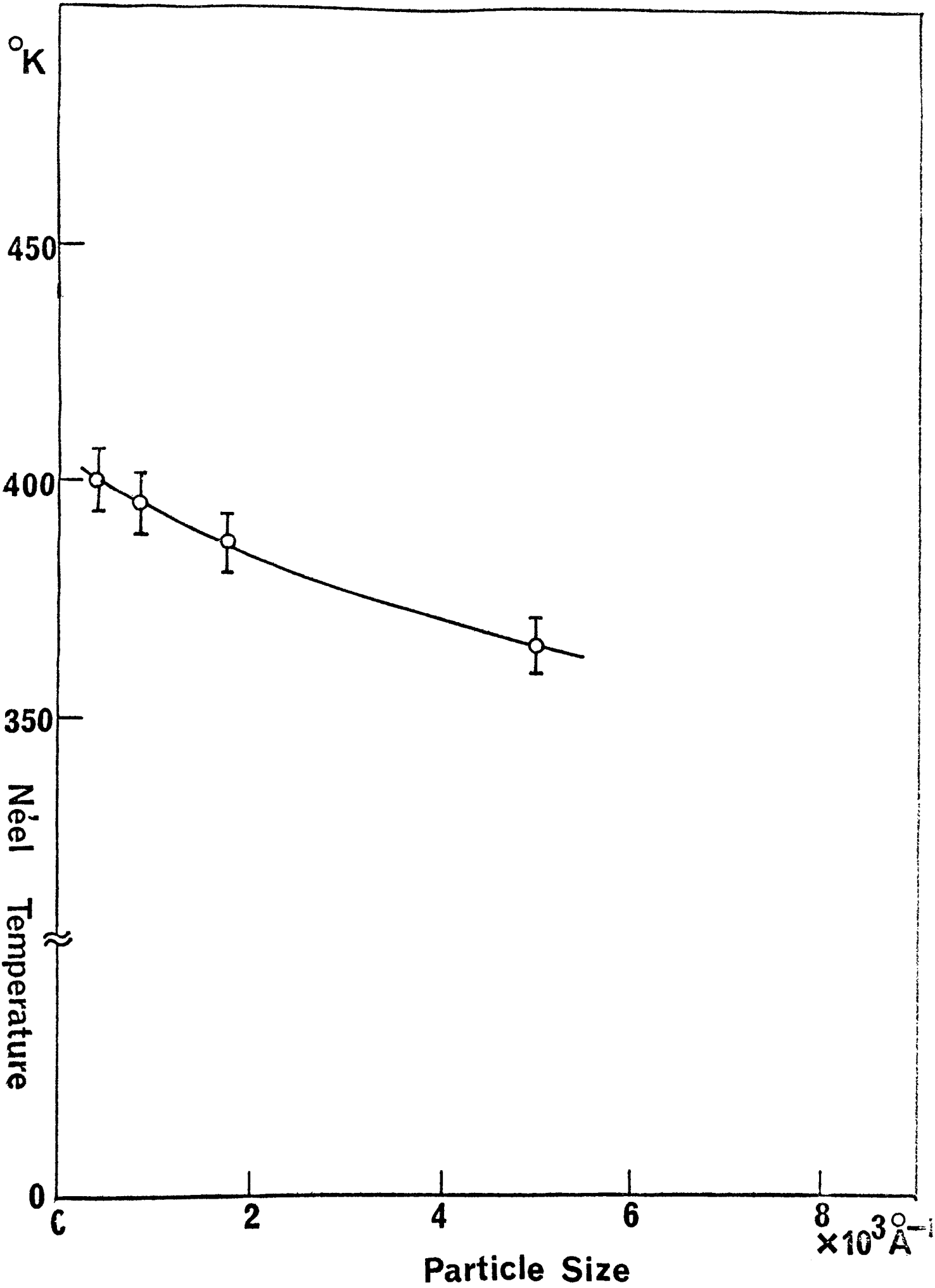

Fig. 6 The observed particle size dependence of the Néel temperature.